

## Ultraviolet Irradiation of Naphthalene in H<sub>2</sub>O Ice: Implications for Meteorites and Biogenesis

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**Abstract** - The polycyclic aromatic hydrocarbon (PAH) naphthalene was exposed to ultraviolet radiation in H<sub>2</sub>O ice under astrophysical conditions, and the products were analyzed using infrared spectroscopy and high performance liquid chromatography. As we found in our earlier studies on the photoprocessing of coronene in H<sub>2</sub>O ice, aromatic alcohols and ketones (quinones) were formed. The regiochemistry of the reactions is described and leads to specific predictions of the relative abundances of various oxidized naphthalenes that should exist in meteorites if interstellar ice photochemistry influenced their aromatic inventory. Since oxidized PAHs are present in carbon-rich meteorites and interplanetary dust particles (IDPs), and ubiquitous in and fundamental to biochemistry, the delivery of such extraterrestrial molecules to the early Earth may have played a role in the origin and evolution of life.

## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are common in carbonaceous chondrites (cf. Cronin *et al.*, 1988; Hahn *et al.*, 1988; Cronin & Chang, 1993), and IDPs (Allamandola *et al.*, 1987; Clemett *et al.*, 1993), and are probably the most abundant and widespread class of organic compounds in the universe (Puget and Leger 1989; Allamandola *et al.*, 1989, 1999). These PAHs are observed to be in the gas phase in a wide variety of interstellar environments, for example, protoplanetary and planetary nebulae, reflection nebulae, HII regions, and the diffuse interstellar medium. However, in dense molecular clouds where temperatures are low ( $T < 50$  K) PAHs, along with most other species, condense onto refractory dust grains (Sandford and Allamandola 1993). The resulting ice mantles can have a variety of compositions, but H<sub>2</sub>O is the dominant species in the ices along most lines-of-sight through dense interstellar clouds (see Sandford, 1996). The presence of PAHs in interstellar ices has been demonstrated by recent astronomical detection of their C-H stretching and out-of-plane bending mode bands in absorption in the spectra of stars embedded within dense clouds (Sellgren *et al.*, 1995; Brooke *et al.*, 1999; Chiar *et al.*, 2000; Bregman *et al.*, 2000). In addition, emission from PAHs has been reported in the coma of comet P/Halley (Moreels *et al.*, 1994).

Kerridge *et al.* (1987) determined that the organic population in the Murchison meteorite contains three or four isotopically distinct components, suggesting a complex history. At least three of these components carry D-enrichment signatures indicative of an interstellar heritage, and PAHs were found to be a major carrier of the deuterium [Kerridge *et al.*'s component C(II)H(II)]. The suite of meteoritic organics examined by Krishnamurthy *et al.* (1992) were observed to have  $\delta D$  values that ranged from about +100 to +1000, with the aromatic fractions having higher values than the aliphatic fractions. There is also evidence that suggests that PAHs may be one of the carriers of deuterium excess in IDPs (Messenger *et al.*, 1995, 1996). These observations all suggest that at least a portion of the PAHs in meteorites have an interstellar origin.

Based on the evidence that PAHs are abundant in interstellar space and in meteorites, and that at least some of the meteoritic aromatics have an interstellar heritage, we have been investigating the UV processing of PAHs in H<sub>2</sub>O ice with an emphasis on exploring the possible connections

between interstellar and meteoritic PAHs. We have previously shown that PAHs undergo both oxidation and reduction photoreactions in ices that result in the production of aromatic hydrocarbon species similar to some of those seen in carbonaceous chondrites and IDPs (Bernstein *et al.*, 1999), and that these same processes can produce large deuterium enrichments in the aromatics (Sandford *et al.*, 2000). Here we describe related studies on the PAH naphthalene ( $C_{10}H_8$ ) with an emphasis on understanding the regiochemistry of the process.

### EXPERIMENTAL TECHNIQUES

The UV irradiation of  $H_2O$ -naphthalene ices were performed in an evacuated sample chamber containing a rotatable  $\sim 15$  K CsI or Ni foil substrate coupled to an infrared (IR) spectrometer that is described in detail elsewhere (Bernstein *et al.*, 1995; Hudgins and Allamandola, 1995). In these experiments, the naphthalene and  $H_2O$  were simultaneously vapor deposited from a finger containing freeze/pump/thawed liquid water and solid naphthalene onto the substrate at a rate that produced an ice layer  $\sim 0.1$   $\mu m$  thick after 30 minutes of deposition (as measured from interference fringes in the infrared spectrum of the sample). After deposition onto the CsI, the  $4000$ - $500$   $cm^{-1}$  ( $2.5$ - $20$   $\mu m$ ) infrared spectrum of the  $H_2O$ -naphthalene ice was measured at a resolution of  $0.9$   $cm^{-1}$  (the observed width of an unresolved line). Analysis of the areas of the resulting infrared absorption bands of both the  $H_2O$  and naphthalene indicates that our sample ice layers typically had  $H_2O$ /naphthalene ratios of  $>100$ . This vapor deposition technique produces intimately mixed ices with the  $H_2O$  in a high density amorphous form that is only observed at low temperatures and pressures, a form that is believed to be representative of  $H_2O$ -rich ices in interstellar molecular clouds (Allamandola and Sandford, 1988; Jenniskens and Blake, 1994; Jenniskens *et al.*, 1995).

After deposition, samples were usually UV irradiated using a microwave-powered, flowing hydrogen, discharge lamp (Warneck, 1962), which produces  $\sim 2 \times 10^{15}$  photons  $cm^{-2}sec^{-1}$ , the flux being nearly evenly divided between the Lyman  $\alpha$  line at  $121.6$  nm and a roughly  $20$  nm wide molecular transition centered at  $160$  nm. Cycles of deposition and photolysis were repeated up to a total of 5 times, depending on sample requirements. Analogous experiments were also carried out in which the samples were continuously co-deposited simultaneous with UV photolysis for up to a week.

In a few experiments, we inserted a  $\text{CaF}_2$  filter in front of the hydrogen lamp during irradiation to block the highest energy photons ( $\lambda < 160$  nm), or we employed a high-pressure xenon arc lamp and water filter, both with and without a glass filter (to remove  $\lambda < 320$  nm) to assess the wavelength dependency of the photolysis.

Following final photolysis, samples were warmed to 160 K at  $\sim 1$  K per minute under dynamic vacuum. The foil onto which the ice was deposited was then removed from the vacuum system under air, placed in a glass vial, and the ice was quickly dissolved in 250  $\mu\text{L}$  of HPLC grade methanol. The sample solution was then separated using High Performance Liquid Chromatography (HPLC). Chromatography was performed on a Hewlett Packard 1100 series HPLC with parallel diode array UV/Vis and fluorescence detectors and a manual injector with a 5  $\mu\text{L}$  loop. Separation was achieved using a Vydac C-18 4.6 x 250 mm 5  $\mu\text{m}$  resin analytical column and a mobile phase of 10% A (methanol) and 90% B (pH 5.5 50mM sodium acetate + 8% methanol) to 40% B in 15 minutes. Elution was monitored by simultaneously measuring both the absorption at 220, 290, and 320 nm and the emission at 325 nm when excited at 220 nm. Observed peaks were identified by co-injection with standards and by comparison of the UV spectrum of the peak of the unknown with that of the standard, both taken *in situ* on the HPLC. Abundances were quantified by calculating the average of the ratio of the area of a given peak at each wavelength to that of a linear fit through zero of the standard at three concentrations.

Comparison of the HPLC measurements demonstrated that the same products were produced in both the samples prepared by ice deposition followed by irradiation and by simultaneous deposition and irradiation. However, simultaneous deposition and irradiation was found to yield products with much higher efficiency, presumably because the molecules in these ices received a more even UV dose and were considerably thicker. Experiments in which we examined the yield for a variety of single-layer irradiation times (0.17, 1, 3, 5, and 12 hours) indicate that the ices co-deposited with simultaneous photolysis were exposed to UV doses equivalent to individual ice layers subjected to  $\sim 30$  minutes of UV per  $\sim 0.1$   $\mu\text{m}$  ice layer. Experiments involving multiple layers gave identical results. These doses fall within the range expected for ices in dense molecular

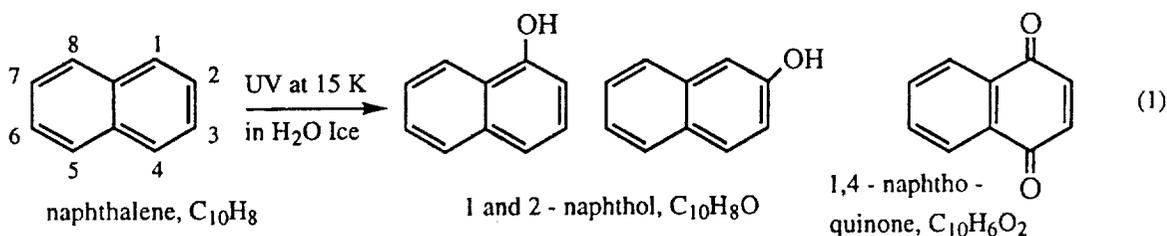
clouds (cf. Prasad and Tarafdar, 1983; Bernstein *et al.*, 1995).

The naphthalene and oxidized naphthalene standards used in our studies were purchased from the Aldrich chemical company: naphthalene, 1-naphthol, 2-naphthol, 1,4-naphthoquinone, 1,2-naphthoquinone, 1,2-dihydroxy naphthalene, 1,3-dihydroxy naphthalene, 1,5-dihydroxy naphthalene, 1,6-dihydroxy naphthalene, 2,3-dihydroxy naphthalene, 2,6-dihydroxy naphthalene, 2,7-dihydroxy naphthalene, 2-hydroxy-1,4-naphthoquinone, and 5-hydroxy-1,4-naphthoquinone. We also used 1,4-dihydroxy naphthalene from the Fluka Chemical Company. No naphthols were detected via HPLC as contaminants in the 99% pure naphthalene. The HPLC grade methanol, sodium hydroxide, and acetic acid for the HPLC buffer were all obtained from Fisher. The water was purified via a Millipore Milli-Q water system to 18.2M $\Omega$ .

Control experiments performed either in the absence of naphthalene or with *unirradiated* H<sub>2</sub>O-naphthalene mixtures did not produce any detectable products. These experiments indicate that the oxidized naphthalene products described below were formed only when H<sub>2</sub>O and naphthalene are exposed together to UV irradiation. Thus, they are not the result of contamination or other nonphotolytic reaction processes.

## RESULTS

Our HPLC analyses demonstrate that the UV photolysis of H<sub>2</sub>O-naphthalene ices results in a mixture of unprocessed naphthalene and oxidized naphthalene compounds (Figure 1). The oxidized photoproducts include both alcohols and ketones. The main products are the two isomers of naphthalene bearing one alcohol (naphthols), and an isomer of naphthalene bearing two carbonyls (1,4-naphthoquinone). The structures of these compounds are shown in Equation 1.



In typical experiments (30 minutes UV per 0.1  $\mu\text{m}$  ice layer), 1-naphthol and 2-naphthol were observed to be produced with approximately 2.5% and 1.4% yields, respectively, relative to naphthalene. 1,4-naphthoquinone, the next most abundant product, is produced with roughly a 0.4% yield relative to naphthalene. The three compounds represented on the right side of Equation 1 make up >97% of all the products of  $\text{H}_2\text{O}$ -naphthalene ice photolysis at  $\sim 15$  K. However, as the UV dose was increased, the yield increased and the ratios of the mono-naphthols approached 1 (at 12 hours of photolysis, the yield was 34% for the 1-naphthol and 27% for the 2-naphthol). At lower doses the yield decreased, but the ratio of 1- to 2-naphthol stayed near 2 (10 minutes of photolysis produced yields of 0.63% for 1-naphthol and 0.37% for 2-naphthol).

Other naphthalenes with multiple oxygen atoms, as well as other unidentified products, are also present, but at lower levels (< 0.1%). We have identified the 2,6- and 2,7-dihydroxy naphthalenes, based on both their retention times and their UV absorption spectra. We have also tentatively identified the 1,3- and 1,5- dihydroxy naphthalenes and 5-hydroxy-1,4-naphthoquinone (Juglone) at 12.9, 9.9, and 16.1 minutes, respectively (Figure 1). We have less confidence in these latter three identifications because of the poor quality of their UV spectra due to contaminating peaks, low abundances, and inconclusive co-injections. We searched for, but were unable to detect, the other oxidized naphthalenes listed in the experimental section. There are a number of small peaks observed in the HPLC trace that we were unable to identify because we were not able to obtain standard samples of all the possible oxidized and reduced naphthalene variants. However, it is reasonable to conjecture that these unidentified species include other dihydroxy naphthalenes, naphthoquinones, and possibly partially hydrogenated hydroxy naphthalenes.

Experiments in which we used a  $\text{CaF}_2$  filter to block the highest energy photons ( $\lambda < 160$  nm) from the  $\text{H}_2$  lamp, and those using a high pressure Xe lamp, produced similar results to the unfiltered  $\text{H}_2$  lamp. This indicates that the formation of these photoproducts does not require Lyman  $\alpha$  or vacuum UV photons. However, when a glass filter was employed to remove  $\lambda < 320$  nm, the light was unable to drive these reactions to any significant degree (<  $10^{-3}$  % yield of naphthols).

In addition, experiments in which we photolyzed the H<sub>2</sub>O-naphthalene samples at 150 K produced similar results to those of our 15 K samples; the alcohols were still the dominant products and 1-naphthol was produced more abundantly than the 2-naphthol. Finally, in experiments in which we photolyzed H<sub>2</sub>O ices containing either of the mono-naphthols, rather than naphthalene, we observed the formation of the other mono-naphthol and unoxidized naphthalene.

## DISCUSSION

### Regiochemistry and Mechanism

In our previous studies of the photochemistry of 11 larger PAHs we concentrated on the fully condensed PAH molecule coronene (C<sub>24</sub>H<sub>12</sub>). Because of its high symmetry, coronene has only one possible mono-alcohol and one mono-ketone isomer (Bernstein *et al.*, 1999). The structure of naphthalene allows for the possibility of two different naphthol, and ten diol, structures (see Equation 1). Thus, while the results presented here are qualitatively in agreement with our earlier work, the regiochemistry is somewhat more complex.

The naphthols were the most abundant products in all our experiments. For realistic doses the 1-naphthol was measured to be consistently about a factor of two more abundant than the 2-naphthol. The dominance of the 1-naphthol is probably a reflection of the greater thermodynamic stability of this isomer, and is consistent with several production mechanisms. However, theoretical calculations (Ricca and Bauschlicher, 2000), the observation of the presence of the naphthalene cation when naphthalene is UV irradiated in H<sub>2</sub>O ice at 15 K (Gudipati *et al.*, 2001), and the invariance in the ratio of produced naphthol isomers with ice temperature are consistent with them arising from a common naphthalene radical cation intermediate, as previously postulated for other aromatics (Bernstein *et al.*, 1999). Our observation that oxidation shuts down when  $\lambda < 320$  nm light is excluded may correspond to the point at which there is insufficient energy to generate the radical cation, but this has yet to be demonstrated.

The UV photolysis of either mono-naphthol in H<sub>2</sub>O ice produced the other mono-naphthol and unoxidized naphthalene. Such a reversible interconversion could provide a path to 1-naphthol (the calculated thermodynamic product), even if the 2-naphthol were formed initially.

## Possible Implications for Meteoritic Aromatics

### *Oxidized Aromatics*

It has long been known that the organic fraction of meteorites contains a major aromatic component (cf. Studier *et al.*, 1972; Hayatsu *et al.*, 1977), and various studies over the years have identified the presence of a host of aromatic molecules, including the molecule naphthalene (cf. Pering and Ponnampereuma, 1971; Basile *et al.*, 1984; Tingle *et al.*, 1991; Kovalenko *et al.*, 1992; Zenobi *et al.*, 1992). To date, relatively little attention has been paid to oxidized aromatics in meteorites. However, the study by Krishnamurthy *et al.* (1992) of the Murchison meteorite does address members of this class of compounds; they list three aromatic ketones: fluorenone, anthracenenone, and anthracenequinone. While the chromatograms presented by Krishnamurthy *et al.* contain unidentified peaks with retention times consistent with naphthols and naphthoquinones, we are unaware of anyone pursuing this by specifically searching for oxidized naphthalenes in meteorites. Any future study that reports the relative abundances of the naphthols and naphthoquinones in carbonaceous chondrites could be instructive regarding the possible role of ice photochemistry as a source of such species.

### *Regiochemistry – Ice Photolysis versus Aqueous Alteration*

Many of the meteorites in which aromatic compounds have been detected have experienced aqueous alteration on their parent body (cf. Zolensky and McSween, 1988). One could imagine that this process might also contribute to the oxidation of PAHs to make aromatic alcohols and ketones. Unfortunately, the oxidation of PAHs in liquid water (in the absence of radiation or air) has received very little study. Thus, it is not currently possible to say whether PAH oxidation would be appreciable under the conditions and timescales of aqueous alteration on asteroidal parent bodies, let alone identifying isomers that would be indicative of this process. However, a project is currently underway in our laboratory to study the rates and products of PAH oxidation in liquid water to determine if there are product isomers or ratios that might distinguish between the oxidized aromatic products of aqueous alteration and ice photochemistry.

Although little is known about the thermal oxidation of naphthalene in liquid water, studies on the photo-oxidation of PAHs in liquid water have been reported in the environmental literature

(Keyeyan and Perez, 1991; Beltran *et al.*, 1995). In contrast to our ice photochemistry results; where the product 1-naphthol is favored, these papers report that the major product of naphthalene photo-oxidation under terrestrial conditions is the 2-naphthol. Thus, it is possible that the relative proportion of 1-naphthol and 2-naphthol in meteorites may provide an indicator of the relative contributions of aqueous alteration and ice photolysis to oxidized meteoritic aromatics.

#### *Deuterium Enrichments in Meteoritic Aromatics*

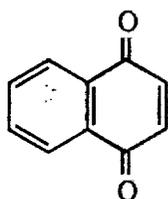
There are a number of processes by which interstellar PAHs can become deuterium enriched, including gas phase ion-molecule reactions (cf. Dalgarno and Lepp 1984; Tielens, 1997), gas-grain reactions (Tielens, 1983, 1997), and unimolecular photodissociation (Allamandola *et al.*, 1987, 1989). In addition, we have recently shown that, in interstellar ices, PAHs can become enriched in deuterium by the same ice photolysis processes that make the oxidized aromatics (Sandford *et al.*, 2000). Each of these various processes is expected to leave a distinctly different signature in the distribution of D enrichment in the PAH population.

Ion-molecule reactions would be expected to preferentially deuterate the *larger* PAHs (Tielens, 1997; Charnley, personal communication), while unimolecular photodissociation should D-enrich only the *smallest* ones (Allamandola *et al.*, 1989). In contrast, in D-enriched interstellar ices (cf. Sandford, 1996; Teixeira *et al.*, 1999), ice photochemistry should produce aromatic deuterium enrichments that are *independent* of PAH molecular size, but which should correlate with specific functional groups, namely the alcohols, ketones, and aliphatic rings produced when PAHs are UV irradiated in H<sub>2</sub>O-rich ices (Sandford *et al.*, 2000).

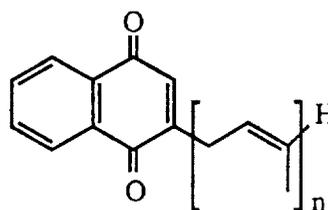
Thus, the regiochemistry of PAH D-enrichment in meteoritic materials, and correlation (or lack thereof) with the presence of specific classes of aromatic compounds could potentially place strong constraints of the relative contributions of a number of different interstellar chemical processes that could have acted on presolar PAHs. In light of the recent work of Sandford *et al.* (2000) and the work reported above, searches for a correlation of D-enrichment with PAH size and oxidation state in meteoritic organics would be of particular interest.

### Astrobiological Implications

The UV photolysis of naphthalene in H<sub>2</sub>O ice produces 1,4-naphthoquinone as the third most abundant product in our ice experiments. 1,4-naphthoquinones, further functionalized, often with a methyl group and a long isoprene chain, play essential roles in biochemistry. While best known as K vitamins and for their role as blood clotting co-factors, naphthoquinones, such as the menaquinones, also perform key biochemical functions in organisms all across the tree of life (Suttie, 1979). Menaquinones often augment or replace ubiquinone or plastoquinone as electron transporters and oxidative phosphorylation co-enzymes. Electron transport and oxidative phosphorylation are absolutely essential processes that are integral to terrestrial metabolism. As one example, the Archaea *Thermoproteus tenax* use menaquinones in the reduction of elemental sulfur to H<sub>2</sub>S as their main energy source (Thurl et al., 1985).



1, 4-Naphthoquinone



Menaquinone

It is possible that the ease of production of 1,4-naphthoquinone and the ubiquity of 1,4-naphthoquinone-based compounds in biochemistry is not a coincidence. Our lab simulations of ice photochemistry suggest a possible connection between the interstellar molecular clouds from which protostellar nebulae form, and meteoritic materials such as quinones and aromatic alcohols. The possibility that these aromatic compounds were delivered to the early Earth by meteorites and IDPs suggests that this connection could have influenced the selection of this class of coenzymes during the origin of life and/or its early evolution.

## CONCLUSIONS

The main products of the UV irradiation of the PAH naphthalene in H<sub>2</sub>O at 15 K are 1- and 2-naphthol, and 1,4-naphthoquinone. For astrophysically relevant irradiations, the yields of these compounds were found to be 2.5%, 1.4%, and 0.4%, respectively. At lower abundance (< 0.1% yield) we have also identified the 2,6- and 2,7-dihydroxy naphthalenes, and possibly the 1,3- and 1,5- dihydroxy naphthalenes and 5-hydroxy-1,4-naphthoquinone (Juglone). A number of other minor photoproducts (< 0.1%) remain unidentified.

The regiochemistry of the UV photoproducts of H<sub>2</sub>O-naphthalene ices is distinctive and can be used to make predictions of the relative abundances of various oxidized naphthalenes that should exist in meteorites if interstellar PAHs contributed to their aromatic inventory. This same interstellar photolysis process is expected to lead to D-enrichment of the aromatics. Thus, if a significant fraction of the aromatics in meteorites have been processed in this manner, one would predict that the deuterium enrichment in meteoritic PAHs should correlate with the presence of reduced PAHs (H<sub>n</sub>-PAHs) and oxidized PAHs (aromatic alcohols and ketones).

While a few oxidized aromatic compounds have been detected in meteorites, this class of molecules has yet to be carefully characterized in meteoritic organics. Thus, a systematic examination of the abundance, D-enrichment, and regiochemistry of oxidized PAHs in meteorites could lead to significant constraints on the interstellar source(s) of meteoritic PAHs and the processes by which they formed and evolved.

Finally, the presence of oxidized aromatic materials in meteorites would be of special interest since these species exhibit interesting biochemical activity and their delivery to the early Earth by extraterrestrial sources could have played a role in the origin and evolution of life.

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## FIGURE CAPTIONS

Figure 1 - The HPLC separation of the material resulting from the UV photolysis of an  $H_2O$ :naphthalene ice at 15 K. The peaks associated with the original naphthalene and the photoproducts 1-naphthol, 2-naphthol, 1,4-naphthoquinone, 2,6-dihydroxy naphthalene, and 2,7-dihydroxy naphthalene are labeled with the corresponding molecular structures.

